NBS REPORT

10 740

FORTY-FIFTH PROGRESS REPORT

to

National Aeronautics and Space Administration

$L.J-13, 3 \ c \ l$

on

Cryogenic Research and Development

Period Ending March 31, 1972

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
Institute for Basic Standards
Boulder, Colorado 80302

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] was established by an act of Congress March 3, 1901. The Bureau's overall goal is to strengthen and advance the Nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the Nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau consists of the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Center for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of a Center for Radiation Research, an Office of Measurement Services and the following divisions:

Applied Mathematics—Electricity—Heat—Mechanics—Optical Physics—Linac Radiation[2]—Nuclear Radiation[2]—Applied Radiation[2]—Quantum Electronics[3]—Electromagnetics[3]—Time and Frequency[3]—Laboratory Astrophysics[3]—Cryogenics[3].

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement, standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; provides advisory and research services to other Government agencies; and develops, produces, and distributes standard reference materials. The Institute consists of the Office of Standard Reference Materials and the following divisions:

Analytical Chemistry—Polymers—Metallurgy—Inorganic Materials—Reactor Radiation—Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations leading to the development of technological standards (including mandatory safety standards), codes and methods of test; and provides technical advice and services to Government agencies upon request. The Institute also monitors NBS engineering standards activities and provides liaison between NBS and national and international engineering standards bodies. The Institute consists of the following technical divisions and offices:

Engineering Standards Services—Weights and Measures—Flammable Fabrics—Invention and Innovation—Vehicle Systems Research—Product Evaluation Technology—Building Research—Electronic Technology—Technical Analysis—Measurement Engineering.

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in improving cost effectiveness in the conduct of their programs through the selection, acquisition, and effective utilization of automatic data processing equipment; and serves as the principal focus within the executive branch for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

Information Processing Standards—Computer Information—Computer Services—Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal Government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System; provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world, and directs the public information activities of the Bureau. The Office consists of the following organizational units:

Office of Standard Reference Data—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

27500-2750400
27503-2750430
27503-2750438
27505-2750550
27506-2750460

March 31, 1972

NBS REPORT

10 740

FORTY-FIFTH PROGRESS REPORT

to

National Aeronautics and Space Administration

on

Cryogenic Research and Development

for

Period Ending March 31, 1972

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado

◁NBS▷

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

TABLE OF CONTENTS

Task status / phase tracking chart (project milestone matrix).

Item No.	Task	Phase / Status (×)	Est. Completion Date	Quart. Report #	page	Task Completed/Terminated
1.	Cryogenic Properties of Solids					
1.1	Thermal Conductivity	Report Composition	7/1/72	44	1	
1.2	Thermal Expansion	—	7/1/72	44	2	×
2.	Slush Hydrogen					
2.1	Heat Transfer (small scale)	Data Analysis	*	44	3	
	Heat Transfer & Mixing	Preliminary Planning	7/1/72	44	3	
	Hydrocarbon Suspension	Apparatus Designing				
3.	Solid Hydrogen Studies	Apparatus Construction	11/1/72	44	10	
4.	Slush Hydrogen Instrumentation	Report Composition				
4.1	Thermal Oscillations	Report in Press	5/1/72	44	16	
5.	Consultation & Advisory Services					
5.1	NERVA Program	Active Coord. with Lewis, MSFC, LASL	**	44	19	
5.2	MSFC Slush H_2 Flow Facility	Active Coord. with Lewis, MSFC, LASL	*	44	20	

Phase of Task (column categories, top to bottom): For Latest Report or Publication on This Task See — Provisional (P) or Final (F); item #; page; Quart. Report #. Est. Completion Date. Report in Press. Report Composition. Data Analysis. Data Taking. Apparatus Construction. Apparatus Designing. Preliminary Planning. Not Started. Active Coord. with Lewis, MSFC, LASL.

* continuing effort
** continuing effort until complete phase-out.

1. Cryogenic Properties of Solids

1.1   Thermal Conductivity of Solids

   1.1.1 General Comments

   The objectives of this program are (1) to measure the thermal conductivities of several aerospace alloys and standard reference materials, and (2) to study the Lorenz ratio of several classes of materials, particularly those which are elemental to structural materials. Temperature range of study is 4 to 300 K.

   During the reporting period, the program was terminated by the sponsor[1] except for the completion of task 2. No further thermal conductivity measurements are funded.

   Personnel contributing during the reporting period were J. G. Hust and L. L. Sparks.

   1.1.2 Program Status

   The Lorenz ratio compilation will be completed a few weeks later than anticipated. Data are now being cross-checked for errors. Upon completion of the cross-check, the data will be plotted and printed as an NBS publication. This will be accomplished in the forthcoming quarter.

1.2   Thermal Expansion

   1.2.1 General Comments

   The objective of this project is to measure the low temperature thermal expansion of materials required by the NERVA program. During the reporting period, the work was terminated by the sponsor[1].

---

[1] Termination of the above programs resulted from a redirection of effort associated with U.S. nuclear rocket development.

2. Slush Hydrogen Heat Transfer and Hydrocarbon Suspension

2.0   General Comments

During this reporting period, activities have been concerned with experiments of heat transfer to slush hydrogen. The hydrocarbon suspension experimental work is complete. The final report of the hydrocarbon suspension work will be included with the report on heat transfer.

Personnel contributing to the program during this reporting period were C. Sindt, G. Suenaga, and J. Hord.

2.1   Slush Hydrogen Heat Transfer

The apparatus used for heat transfer experiments is the same basic system that was used for hydrocarbon suspension work. The experimental vessel is a 10 cm diameter dewar approximately 30 cm deep. This dewar is enclosed in a 15 cm diameter dewar which is filled with liquid hydrogen and pumped to a pressure corresponding to the experimental pressure. The bath dewar is thermally shielded with liquid nitrogen in a surrounding 25 cm diameter dewar.

The heat transfer unit is mounted in the 10 cm diameter experimental dewar on a 0.95 cm stainless steel thin-wall tube.

2.1.1   Slush Hydrogen Heat Transfer Unit

The heat transfer unit consists of a 2.54 cm diameter cylindrical block of electrolytic tough pitch copper. The cylinder is 1.9 cm long and is drilled in six places to accept carbon resistors, which are embedded in a high thermal conductivity epoxy. They are connected in parallel and have a resistance of 13.865 ohms at 20 K.

Soldered to the undrilled face of the copper cylinder is a 0.05 mm thick stainless steel sheet, the heat transfer surface. The heater block is vacuum jacketed except at the heat transfer surface.

2

The stainless steel sheet extends across a 3.1 mm space between the heater and the vacuum jacket and is soldered to the jacket, thus providing the vacuum seal.

In the center of the heater cylinder, 0.25 mm below the heat transfer surface, is a thermocouple, embedded in a low melting temperature metallic eutectic to assure good thermal contact. A second thermocouple is similarly mounted at a radius of 1.96 cm, centered between two of the resistance heaters.

An array of twelve thermocouples extends out from the heater surface, spaced at approximately 1.1 mm intervals. Four of the thermocouples are located on the heater center line, four at about 1/2 the heater radius, and the other four at the heater edge. All of the thermocouples are Chromel vs. gold (0.07 atomic percent iron).

The mounting tube for the heater is used as the vacuum pumping line and a good insulating vacuum is maintained at all times. This tube is also used as the conduit for the power leads and the voltage measurement leads for a distance of about 30 cm. The leads are therefore in a vacuum environment within the experimental vessel. The leads pass through a hermetic seal at the top of the experimental vessel and are then enclosed in a second tube about 1 m long (filled with helium gas). This tube is coiled in the hydrogen bath dewar and is submerged in the hydrogen. Submerging the assembly in the pumped hydrogen bath intercepts all of the heat transferred down the leads before it enters the experimental vessel or the heater unit.

A second thermocouple array was initially located at the surface in the experimental vessel, but it interferred with slush preparation. Also, it was not useful as the surface temperature remained the same as the bulk temperature in all but one of the experiments. In this experiment, the surface liquid thermal stratification data were

3

not meaningful as they were dependent on the frequency of slush preparation and this was a random occurrence depending on many other test operations.

2.1.2 Heat Transfer Test Procedure

Four types of tests have been conducted using three orientations of the heater surface. The four tests were: 1) heat transfer at one atmosphere pressure in liquid at normal-boiling temperature, 2) heat transfer at triple-point pressure in liquid, 3) heat transfer at triple-point pressure in settled slush (estimated settled solid fraction of 0.45), and 4) heat transfer in settled slush at one atmosphere pressure using helium gas as the pressurizing gas. The three orientations of the surface were horizontal facing up, vertical, and horizontal facing down.

The test procedure for the three orientations of the heater was identical for each of the four types of tests.

For the test at one atmosphere pressure of normal-boiling liquid, the entire volume of liquid was brought to temperature, including the bath, by controlling the pressure at $101.3 \pm 0.3 \, kN/m^2$ (760 torr) with a barostat. The liquid was then mixed until no change in pressure occurred during mixing and until bubbles formed and did not collapse near the dewar bottom. Thermocouples were then read for a base point. Power was supplied to the heater with a d-c power supply which maintained voltage constant within $\pm 0.2\%$. The voltage at the heater was recorded as well as the voltage drop across a calibrated resistor in series with the heater power leads. The power was calculated from the voltage and current (calculated) across the calibrated resistor. The thermocouple signal was amplified 1000 times and recorded automatically on magnetic tape with a data acquisition system. Pressure was maintained at the set value using the

4

barostat, while the voltage to the heater was increased in steps to cover the heat transfer range from 0.002 W/cm^2 to the point where the boiling regime changes from nucleate to film (burn-out). The heating rate was increased in steps to maximum, then decreased in steps to determine hysteresis effects, if any.

The procedure for tests of triple-point liquid was to pump the dewar pressure to triple-point and maintain it at triple-point using the barostat for pressure control. The remainder of the test was similar to the procedure for testing normal-boiling liquid.

The procedure for heat transfer to slush at triple-point pressure was to prepare slush in the experimental dewar using the freeze-thaw method until the dewar was filled with settled slush. The pressure was then maintained at triple-point during the test. Heat was increased and decreased during the test, as it was for the liquid tests, but burn-out was not defined, as the solid in the slush would not last long enough to determine the burn-out heat rate with any certainty. Therefore, the maximum heat rate used in the slush tests was the same as for triple-point liquid.

For the slush pressurized to one atmosphere pressure, the procedure was similar, except that after slush preparation and prior to adding heat, the pressure was raised to one atmosphere by introducing cold helium gas and the pressure was maintained during the test. This test was always run last so that the liquid used in the other tests was not saturated with helium gas.

For both slush hydrogen tests, the slush had to be replenished frequently, thus interrupting the increasing or decreasing heat rate. To keep the data consistent after slush preparation, the heat rate was always increased from a lesser value during the increasing heat flux tests and was decreased from an arbitrary larger value during the

decreasing heat flux tests. During the higher heat flux tests, slush had to be prepared prior to each flux test point to assure adequate slush depth over the heater during the data taking period.

The thermocouple used for an absolute temperature reference was located at the bottom of the experimental vessel. In this location, the absolute temperature was known for each test — as the thermocouple was below the heater, it remained in normal-boiling liquid during the normal-boiling liquid tests, and during the triple-point liquid tests, it remains in triple-point temperature liquid. During the slush tests, the thermocouple was always surrounded by slush so it was at triple-point temperature.

2.1.3 Test Results

Data have been taken for the four types of experiments using all three orientations of the heat transfer surface. The data for the surface facing up have been reduced to the form of heat transfer rate per unit area versus the difference between the heater block temperature and the bulk hydrogen temperature. These data are presented in figure 2.1.1; they have not been corrected for temperature drop across the 0.05 mm stainless steel sheet or for surface heat loss due to the fin effect of the stainless steel sheet that extends beyond the copper block to the vacuum jacket. These corrections are both small but they will be made in the final data analysis; therefore, the data presented in figure 2.1.1 are preliminary.

For the purpose of comparison, a curve from Cooling and Merte[1] is shown for the same configuration of heat transfer unit at a pressure of 117 kN/m^2 (878 torr). Agreement is reasonable over the

---

[1] Cooling, K. J. and Merte Jr., H., Incipient and nucleate boiling of hydrogen, ASME Paper No. 68-WA/PID-4, Presented at ASME Winter Annual Meeting, New York, N.Y. (Dec. 1-5, 1968).
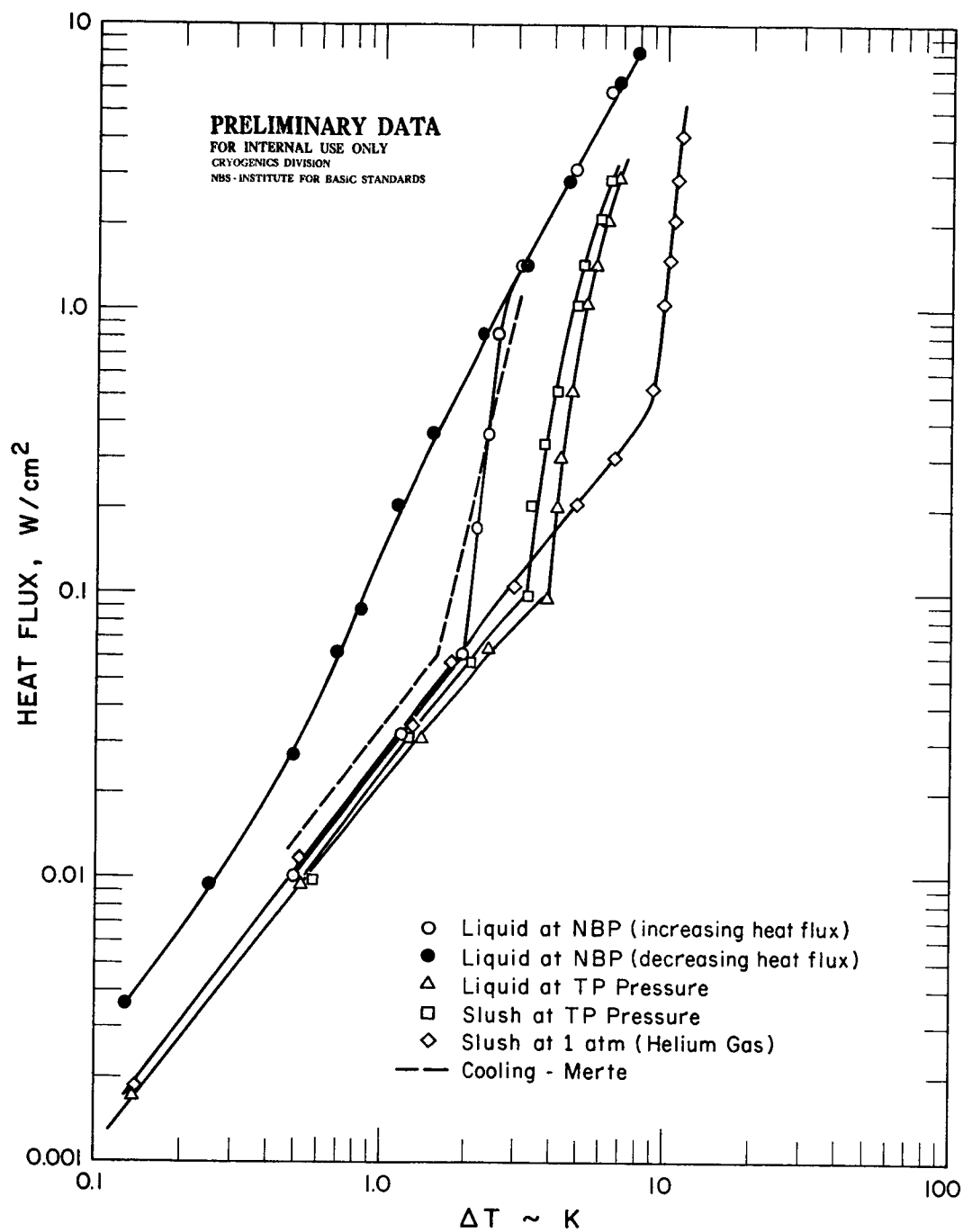
Figure 2.1.1 Preliminary Data For Heat Transfer In Hydrogen,
Horizontal Surface Facing Up.

7

range of data presented for the case of increasing heat flux. However, the hysteresis effect shown in the data for decreasing heat flux was not present in Cooling and Merte's work with a polished stainless steel surface. Their values for rougher surfaces did indicate a hysteresis effect similar to the data shown by closed symbols, however. The point where vapor first appears on the surface occurs when the curve changes slope and also is in agreement with Cooling and Merte's experimental results. No data are available for reasonable comparison with the other three curves.

Decreasing heat flux data for triple-point liquid, triple-point slush, and slush at one atmosphere pressure are not shown as they did not have hysteresis effects (even though, in the case of the triple-point liquid, vapor sites were visible down to a temperature difference of 1 K).

Vapor became visible in the triple-point pressure slush on increasing heat flux at the point where the curve changes slope. As the heat flux was increased and more vapor bubbles formed, local mixing of the slush occurred over the heat transfer surface as the bubbles rose in the liquid. This mixing commenced at about 1.5 W/cm^2 heat flux. In the slush pressurized to one atmosphere, no bubbles were ever observed even though the curve does change slope as do the others; however, vapor may have formed and collapsed very close to the surface and not been visible. Visibility in the slush is very limited. Because vapor bubbles did not remain and travel to the surface, no mixing occurred at this condition.

The data for the other two orientations of the heater unit are being reduced to curves similar to those shown in figure 2.1.1 and will be presented in the next progress report. Also, reduced data from the thermocouple array will be presented.

3. Solid Hydrogen Studies

3.0   General Comments

Personnel contributing during this period were D. E. Daney, R. O. Voth and L. M. Anderson.

3.1   Experimental

A detailed design of the hydrogen freezing apparatus has been completed and a number of the components have been procured or fabricated. An assembly drawing is shown in Figure 3.1.1. An additional liquid nitrogen shield dewar and plexiglass safety shield will be used, but are deleted from this drawing to avoid confusion. The basic features are:

3.1.1 Hydrogen System

1. A hydrogen freezing chamber (bottom). The walls of that chamber will be made of 0.005 inch Mylar to minimize thermal resistance while allowing a clear view of the freezing hydrogen.

2. A standpipe located above (and connected to) the freezing chamber, to serve as a liquid hydrogen reservoir during freezing. The fall in liquid level, as indicated by the capacitance level gage, will provide an indication of the reduction in volume of the hydrogen in the freezing chamber. From this liquid level reading, the mass of hydrogen solidified and the rate of freezing at a given time can be determined. The freezing rate will provide one indication of the heat flux. A heater on the standpipe will prevent solid hydrogen blockage of the passageway leading into the freezing chamber.

Legend for Figure 3.1.1:

1. Helium Blower Motor.

2. Helium Blower Shaft.

3. Liquid Hydrogen Radiation Shield.

4. Helium Blower Impeller.

5. Internal Gear.

6. Helium Flow Control Valve.

7. Liquid Helium Bath.

8. Direction of Helium Gas Flow.

9. Heater.

10. 6-Inch I.D. Pyrex Dewar.

11. Flow Meter (Venturi in Final Design).

12. Dewar Vacuum Space.

13. Heat Exchanger (4-1/8 O.D. x 0.095 inch wall copper tube with 3/8 inch fins at 1/4 inch spacing outside, ribbon packing inside).

14. Fill Line Heater.

15. Co-Axial Capacitor Leads.

16. Vacuum or He Transfer Gas.

17. Fill Line.

18. Standpipe with Concentric Tube Capacitor for Liquid Level Meas.

19. Vacuum.

20. Liquid Hydrogen.

21. Heater.

22. 4-Inch Pyrex Dewar With Stainless Steel-to-Pyrex Joint.

23. Foam.

24. Pyrex Baffle.

25. Germanium Thermometer.

26. Gold Iron vs. Copper Differential Thermocouple (Typical).

27. Freezing Hydrogen.
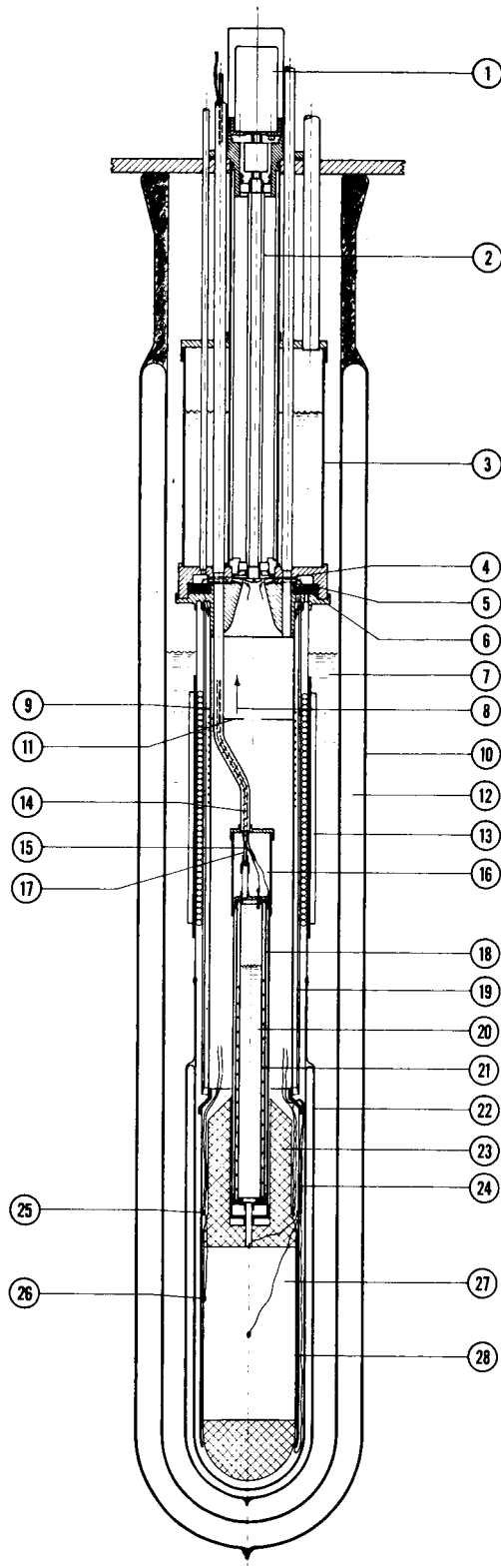
28. 82 mm O.D. x 0.005 Inch Mylar Cylinder.

Figure 3.1.1 Hydrogen Freezing Apparatus

10a

3. A hydrogen chamber at the upper end of the apparatus to act as a radiation shield and a source of precooling refrigerant.

3.1.2 Helium Refrigerant System

1. The liquid helium bath will provide the refrigeration for freezing the hydrogen.

2. The variable speed blower will circulate helium heat exchange gas by variable paths as indicated by the arrows in Figure 3.1.1.

3. A rotary valve at the blower discharge allows a choice or combination of two possible paths for the helium gas, thus controlling the helium gas temperature and the freezing rate: For maximum refrigeration, all of the flow may be diverted through the ribbon packed heat exchanger communicating with the liquid helium bath. For minimum refrigeration, the flow may be routed through the inner passage which is insulated from the liquid helium bath. This passage is also provided with a heater to enable thawing the hydrogen. Intermediate degrees of refrigeration may be obtained by splitting the helium gas stream in any proportions desired.

3.1.3 Hydrogen-to-Helium Gas Heat Exchange System

Cold helium gas is routed around the outside of the pyrex baffle, then upward next to the freezing chamber. Refrigeration is restricted, as far as possible, to the vertical walls of the freezing chamber by means of the foam insulating blocks and vacuum jackets surrounding the liquid and gaseous hydrogen containers.

11

3.1.4 Helium Gas Flow Measurement

Just before helium gas re-enters the circulating blower, it will pass through a metering orifice. The measured flow rate combined with temperature measurements upstream and downstream of the freezing chamber will allow a second determination of freezing heat flux.

3.1.5 Instrumentation

1. Germanium thermometer, designated T_o in Figure 3.1.1, for absolute temperature indication in helium gas stream downstream of the freezing chamber. A thermocouple reference junction also will be located at this point for use in differential temperature measurements at other points.

2. Gold (0.07 at. % Iron) vs. Copper junctions: No. 1 - inside freezing chamber wall temperature; no. 2 - freezing chamber center temperature; no. 3 - standpipe exit temperature; no. 4, 5, and 6 - helium gas temperature difference upstream-to-downstream of freezing chamber.

3. A hydrogen liquid level capacitance gage.

4. Helium gas flow orifice upstream and downstream pressure taps.

3.1.6 Photography and Visual Observation

These will be important for determining the clarity and uniformity of solid hydrogen formation. Photography through the seven pyrex walls, the Mylar freezing chamber, plexiglass shield, and the helium and nitrogen baths presents some problems; however, good quality motion pictures have been achieved under similar conditions at this laboratory.

12

3.1.7 Components which have been Fabricated or Procured

1. All parts of the liquid hydrogen standpipe including the capacitance gage.

2. The helium liquid-to-gas heat exchanger.

3. The pump assembly including impeller, diffuser, shaft, and motor have been procured from an outside vendor.

4. The hydrogen radiation shield vessel and top mounting plate have been assembled.

5. The three pyrex dewars and pyrex baffle have been procured.

4. Slush Hydrogen Instrumentation

4.0 General Comments

Contributing to the program during this reporting period was R. S. Collier.

4.1 Thermal Oscillations

The final report on thermal oscillations has been completed and is now in press. It will be available in the next quarter, and it is planned to excerpt various sections for publication in several technical journals.

5. Consultation and Advisory Services

5.0   General Comments

Contributing personnel were J. Hord, P. R. Ludtke and A. F. Schmidt.

5.1   NERVA Program

On February 28, discussions were held with D. J. Miller (SNSO-Hq), E. H. Hyde and H. Attaya (NASA-MSFC) on the redirection of NERVA contract work and the increased emphasis of NBS efforts on the MSFC Slush Hydrogen Flow Facility (see Section 5.2). Our services have also been offered to the Los Alamos N-Division in whatever manner deemed beneficial to the LASL nuclear propulsion program.

At the request of the sponsor, a report entitled "Solid Hydrogen as a Space Storable Propellant — A Preliminary Study" has been prepared and is appended to this progress report.

5.2   MSFC Slush Hydrogen Flow Facility

Several letters have been sent to L. Worlund, Z. Adamson, and B. Farley giving advice on pressure and helium purge taps, valve stem leakage problems and seal design, and design criteria for indium coated O-ring seals.

On February 17, P. Ludtke attended a meeting at the NASA-Marshall Space Flight Center with E. H. Hyde, T. Marshall, B. Farley, and D. Hutson to discuss problem areas of the MSFC slush flow facility. Detailed drawings of an NBS recommended pressure tap, a pressure relief tap, a helium inerting tap, a valve bonnet seal, and a transfer line see-thru section with sapphire windows were provided by Ludtke and discussed at the meeting. Design information and criteria from the above drawings will be used in designing the slush transfer line piping for the MSFC flow facility. In addition,

P. Ludtke has been working on the design of a slush hydrogen generator to be incorporated into the MSFC flow facility. Drawings and specifications for the vessel, including stirring motor mount and window assemblies, are being prepared.

APPENDIX

SOLID HYDROGEN AS A SPACE STORABLE PROPELLANT
-- A PRELIMINARY STUDY

J. Hord

1. INTRODUCTION

Because of its low molecular weight, high heat capacity, and high specific heat ratio, hydrogen is the propellant chosen for a variety of chemical and nuclear rocket vehicle applications. It has long been recognized [1,2][†] that subcooled liquid hydrogen, slush hydrogen, and solid hydrogen can extend the duration of space missions. By subcooling liquid hydrogen, or solidifying a portion of it, the propellant bulk density and heat capacity are increased, resulting in significant payload advantages. The <u>exact</u> extent of these advantages is predictable only for specific mission requirements; however, it is apparent that increasing propellant bulk density and heat capacity can 1) increase thrust-to-weight ratio, 2) extend mission duration, and 3) reduce in-orbit or refuel station storage system weight. Related advantages are reductions in tank insulation requirements, tank venting frequency, tank size and weight, and possibly increased vehicle reliability.

As always, we must be willing to sacrifice something to obtain the benefits of the higher density hydrogen -- in this case it is ease of handling. The subcooled liquid hydrogen can be prepared prior to ground-launch by vacuum pumping. This operation could be conducted safely, with minimal effort and sacrifice in ease of handling. Launch-site preparation of slush hydrogen is somewhat more complicated and is

---

† numbers in brackets indicate references at the end of this paper.

not yet state-of-the-art technology; however, laboratory-sized facilities have proven feasible [3], and a large-scale slush generating and flow facility is scheduled for operation at MSFC in the latter part of 1972. In low g environments subcooled liquid and slush hydrogen require some sort of mixing device, i.e., to take full advantage of the increased heat capacity all heat leak (thermal energy) must be uniformly distributed throughout the fluid.

Recently, there has been some discussion on the feasibility of using solid cryogen propellants in certain vehicle applications. Such propellants, thawed upon demand, could conceivably be used as structural members [4], resulting in greater reductions in vehicle weight. Solid hydrogen offers the ultimate in bulk density and heat capacity for hydrogen-propelled nuclear and chemical rockets. Consequently, solid hydrogen -- as compared to liquid or slush hydrogen -- offers the maximum storage life in earth/lunar orbit and space-journey propellant tanks. Certain propellant management and structural advantages are readily apparent, e.g., reduction in over-board vent losses, reduced sloshing effects and possibly use of the solid hydrogen as a load-bearing material. These advantages will be compromised to some extent by the necessity to thaw the solid hydrogen, upon demand, at a controllable rate. Thawing techniques, using chemical or nuclear energy, will have to be optimized and present a design challenge. It is anticipated that the hydrogen should be frozen in modular contained units, e.g., a shuttle cargo tank filled with a monolithic block of solid hydrogen.

A preliminary feasibility study, under the sponsorship of SNSO, is in progress at NBS-Boulder. The specific goals of this study are to 1) calculate the freezing and melting rates of hydrogen for various geometries, refrigerant temperatures, and refrigerant heat transfer

coefficients, 2) to measure hydrogen freezing and melting rates for a simple geometry such as a cylinder, and 3) to develop freezing techniques which yield a uniform and high density solid.

Should this study prove that preparation and thawing of solid hydrogen is feasible and predictable, we must be prepared to make mission design tradeoffs, i. e., do the advantages of using solid hydrogen outweigh the disadvantages. At this point it is believed that the disadvantages will consist mostly of increased handling complexity and refrigeration costs (for solidification of H_2). Thus, the storage characteristics of solid hydrogen in a space environment are of paramount interest to us and the remainder of this paper is devoted to that topic.

2. STORAGE CHARACTERISTICS OF SOLID HYDROGEN IN A SPACE ENVIRONMENT

A cursory examination of the literature indicates that studies have concentrated on the storage of liquid hydrogen in a space environment, while slush and solid hydrogen have drawn little attention. This is understandable because it has not yet been demonstrated that slush or solid hydrogen can be safely and easily handled in large quantities. The 'apparent' advantages [2] of slush or solid hydrogen provide a strong stimulus to extend existing propellant management technology to these higher density propellants. So that we may clearly appreciate the advantages of solid hydrogen as a propellant for lunar and inter-planetary missions, we will examine the storage characteristics of solid hydrogen in a space environment.

To obtain estimates on the storage durability of solid hydrogen we must specify the storage conditions. This requires detailed knowledge concerning solar radiation flux, albedo, planet-shine, insulation quality, reflective coatings, vehicle attitude control, vehicle geometry, propellant tank vent pressure, etc. These conditions will obviously

vary with each mission, i.e., whether the vehicle operates in earth or lunar orbit or interplanetary space. We could systematically vary each of the foregoing parameters and perform a parametric study; however, because of the preliminary nature of this paper we shall restrict our attention to a few simple examples that adequately bracket the storage problem. First we shall consider relatively low earth-orbit storage and then interplanetary space storage.

2.1 Earth orbit storage

We shall arbitrarily specify that the earth orbit is ≈ 100 (~ 185 km) nautical miles. This orbit is chosen so that we may simplify our calculations by considering the vehicle environment as an infinite sink for both radiant heat flux and gaseous hydrogen venting, i.e., 1) outer space is considered an infinite black void with an effective temperature of ≈ 4 K and 2) gas molecules leaving the vehicle will not be reflected back to the vehicle. The latter point is the real reason for choosing an orbit of 100 nautical miles. At this altitude the mean free paths of the atmospheric constituent gases are large enough [5] to assure rare collisions with the vehicle and gases escaping from the vehicle. Atmospheric pressure at this altitude is about 10^{-6} torr, and the corresponding mean free paths of the atmospheric gases are about 100 meters. We shall now examine three separate cases for earth orbit storage.

Case I: We shall assume that the current state-of-the-art technology, for well insulated spacecraft, will reduce solar radiation, albedo, etc., to $\sim 10^{-4}$ W/cm^2 net heat flux to the stored cryogen. Solar radiation plus albedo is normally taken as about 0.2 W/cm^2 incident heat flux. Thus, ~ 0.05 of one percent of the incident heat flux is absorbed by the cryogen. Experience indicates that solar-shielded vehicle equilibrium temperature is normally around 300 K. Using a multilayer

insulation (15 to 20 layers/cm) of 5 cm thickness, the net heat flux should not exceed 10^{-4} W/cm^2. Then for this case, we assume solar-shielded state-of-the-art multilayer insulation, spinning-vehicle attitude control, no refrigeration devices onboard, and the cryogen is stored (vented) at ~1.6 atm absolute pressure. We shall further assume that the thermal energy (10^{-4} W/cm^2) is uniformly deposited throughout the bulk of the stored cryogen. The temperature of the solid hydrogen will be taken at 13 K, just below the triple point (13.80 K).

It will be instructive, for this case, to compare the relative merits of subcooled liquid, slush, and solid hydrogen. The change in enthalpy for these various physical phases of hydrogen propellant are given in table 1. The advantages of using subcooled or solid hydrogen are quite apparent for both the zero-loss and vented-tank conditions. For a specified net heat flux the storage time is directly proportional to the available enthalpy change as indicated in table 1. Thus solid hydrogen has a storage durability of 567.8/453.9 $\approx$ 1.25 times that of NBP liquid hydrogen. Perhaps more importantly, solid hydrogen will endure 132.1/18.2 $\approx$ 7 times as long as NBP liquid hydrogen before overboard venting is required.

Next we examine the improvement in bulk density with solidification. Again, from table 1 there is a significant increase in bulk density as the liquid hydrogen is subcooled or partially/totally solidified. Thus, more hydrogen can be packed onboard volume-limited vehicles such as the shuttle cargo tank. Approximately 23 percent more fuel mass could be transported, in a given size tank, if solid hydrogen is used rather than NBP liquid hydrogen.

From the foregoing discussion, we see that a solid hydrogen fueled vehicle could thaw and burn 23 percent of its cargo and still retain a storage durability that exceeds (by 25 percent) an identical liquid (NBP) hydrogen fueled vehicle.

Table 1. Tabulated values of bulk heat capacities and corresponding storage durabilities for various physical forms of hydrogen.

Physical form* of hydrogen (as launched)	Column 1 $\left(\dfrac{W\text{-}s}{g}\right)$	Column 2 $\left(\dfrac{W\text{-}s}{g}\right)$	Column 3 (g/cm^3)	Column 4 (days)	Column 5 (days)
saturated liquid @ 1 atm (NBP)	18.2	453.9	0.071	73	1812
triple point liquid	71.8	507.5	0.077	287	2026
50% solid (slush)	100.9	536.6	0.082	403	2142
100% solid (@ 13 K)	132.1	567.8	0.087	527	2267

Column 1: Available enthalpy change from the enthalpy state of H_2, as launched, to the enthalpy state of saturated liquid H_2 @ 1.6 atm (22 K), i.e., no venting (zero-loss storage of H_2).

Column 2: Available enthalpy change of column 1 plus the latent heat of vaporization at 1.6 atm (22 K), i.e., energy absorbed per gram of H_2 vented.

Column 3: H_2 density (as launched).

Column 4: Storage duration for zero-loss of H_2 (no overboard venting).

Column 5: Maximum storage duration for total vaporization of liquid and/or solid H_2 (tank vents at 1.6 atm).

*Note: It is assumed that the same mass of H_2 is launched, irrespective of the physical form.

To obtain estimates of actual storage times, we must specify the tank volume and its thermally irradiated area. This volume/area ratio varies widely with mission, orbit, attitude control, etc. We will assume a cylindrical tank configuration with $L/D = 4$ and broadside thermal irradiation, i.e., the thermally irradiated area is LD. This is a worst case, as the tank would optimally be positioned so that the exposed area is $\pi D^2/4$. Assuming a tank diameter of about 7 meters we calculate a volume/area ratio of ~ 500 cm^3/cm^2. Using a net heat flux of 10^{-4} W/cm^2, we find that 10^{-4} watts of thermal energy are delivered to 500 cm^3 of cryogen. The density of saturated liquid hydrogen at 1.6 atm is 0.069 g/cm^3; therefore, 10^{-4} watts are delivered to 0.069 x 500 = 34.5 grams of hydrogen. Now, by using the heat capacity data in column 2 of table 1, we may calculate the time required to totally vaporize the hydrogen propellant. For solid hydrogen this time is ≈ 2267 days (see column 5 of table 1). From table 1 we note that 567.8 (W-s) are required to vaporize a gram of solid hydrogen, but 132.1 (W-s)/g may be absorbed without loss of propellant. Then hydrogen may be stored for (132.1/567.8) x 2267 = 527 days without loss of propellant if 13 K solid is placed in orbit. Storage times for the slush and liquid propellants are proportionally lower as indicated by the data in table 1.

Case 2: Next we consider the storage of solid hydrogen, vented to the atmosphere, in a 100 nautical mile earth orbit. The conditions of storage are identical to those of Case 1, except that the tank is vented to $\sim 10^{-6}$ torr. This storage condition would be imposed if the storage tank were inadvertently or intentionally vented to the atmosphere. Table 2 indicates the saturation vapor pressure, specific enthalpy, density, and heat of sublimation of solid hydrogen at various temperatures. It is readily apparent that the vapor pressure is extremely low

Table 2: Tabulated properties of solid hydrogen

Temperature (K)	Saturation Pressure (torr)	Heat of Sublimation $\left(\frac{W\text{-}s}{g}\right)$	Specific Enthalpy $\left(\frac{W\text{-}s}{g}\right)$	Density (g/cm^3)*
13.803	52.8	508	10.6	0.08663
13.00	30.1	503	8.4	.08686
12.00	13.8	495	6.2	.08716
11.00	5.6	487	4.4	.08743
10.00	1.9	478	3.1	.08768
9.00	.53	469	2.0	.08793
8.00	.11	460	1.3	.08816
7.00	1.56×10^{-2}	450	0.7	.08839
6.00	1.20×10^{-3}	440	0.4	.08861
5.00	3.57×10^{-5}	430	0.2	.08882
4.00	2.08×10^{-7}	420	0.1	.08904
3.00	4.83×10^{-11}	409	0.02	.08925
2.00	3.99×10^{-18}	399	0.005	.08946
1.00	8.26×10^{-39}	389	0.0003	.08967

* - Extrapolated from ref [6]. All data in this table taken from references [6, 7].

A-8

at temperatures below 4 K. Also, the heat of sublimation steadily declines with decreasing temperature. Note that the density increases only 3 percent between 13 K and 1 K. Also, the specific enthalpy of the solid is reduced by only 8.4 (W-s)/g between 13 K and 1 K. This increase in heat capacity is only 1.7 percent of the heat of sublimation at 13 K and only 1.5 percent of the available enthalpy change between 13 K and 22 K (column 2 of table 1). Thus, it is obvious that little is to be gained by intentionally reducing the solid temperature below 13 K. Furthermore, rejection of heat by sublimation will result in a greater loss of propellant at the lower temperatures (as a result of the lower heats of sublimation). The latter point will become apparent as we proceed with our sublimation calculation.

Let us now consider the problem of solid hydrogen subliming in a storage tank that is vented to a 10^{-6} torr environment. As previously explained, it is assumed that hydrogen molecules leaving the tank are lost forever. We shall also assume that the flow conductance of the vent plumbing is sufficiently large to permit the hydrogen vapor pressure in the tank to equilibrate near 10^{-6} torr. Then the solid-vapor interface exposed to the tank ullage will rapidly assume an equilibrium temperature corresponding to $\sim 10^{-6}$ torr. Some time will then be required for the bulk of the solid to attain thermal equilibrium at this lower temperature. The solid block must cool by thermal conduction of internal heat to the solid-vapor interface where sublimation is taking place. In reaching this lower equilibrium temperature some propellant will be vaporized -- this loss of propellant will be referred to as 'flashing loss'. We shall assume that the time required to incur this flashing loss is small in comparison to the in-orbit storage time.

Additionally, we will require that all thermal energy is deposited at the subliming solid-vapor interface, and that this radiant energy does not significantly affect this interface temperature. In this way, we avoid thermal conduction problems in the solid hydrogen and can perform a two-step steady state calculation. First we compute the 'flashing loss', then the sublimation losses attributable to the steady state radiant heat flux. All of these losses will be computed at the solid-vapor interface where the temperature and heat of sublimation were lowered at the instant the vent valve was opened. Effectively we are assuming that all sublimation takes place isothermally at the reduced temperature, i.e., an isenthalpic thermodynamic process is assumed.

From table 2 we note that the equilibrium temperature of solid hydrogen at 10^{-6} torr is about 4.5 K. To allow 1) for some temperature rise at the solid-vapor interface due to thermal irradiation, and 2) for some resistance to vapor flow through the vent valve, we select a temperature of 5 K. The heat to be removed from the solid hydrogen between 13 K and 5 K is 8.2 (W-s)/g and the heat of sublimation at 5 K is 430 (W-s)/g. Then the initial flashing loss will be (8.2/430)100 = 1.9 percent, and 98.1 percent of the initial mass remains to be vaporized at 5 K.

Following the same procedure as in Case 1 we impose 10^{-4} watts of thermal energy on 500 (.981) cm^3 of solid hydrogen. With a hydrogen density of 0.08882 g/cm^3 our thermal flux is $(10^{-4})/(500 \times .981 \times 0.08882) = 2.3 \times 10^{-6}$ W/g. Then the time required to totally vaporize the solid hydrogen at 5 K is $430/(2.3 \times 10^{-6})$ = 1.87×10^8 seconds, or 2164 days.

While this storage time is lower than that of Case 1 the comparison is not yet a direct one. In Case 1 we restricted the initial mass of

solid hydrogen to be identical with those for liquid and slush hydrogen; therefore, we could make direct comparisons with liquid, subcooled liquid, and slush hydrogen storage. Correcting Case 2 to the same initial mass, as was used in Case 1, we obtain a storage duration of 1684 days -- considerably less than the 2267 days for Case 1. The 1684 day storage time could have been derived by simply taking the ratio of available enthalpy change, i.e., $[(430 \times .981)/(567.8)]2267 = 1684$ days.

It is apparent that vented storage of solid hydrogen in-orbit reduces storage durability, and does not significantly improve the bulk density or bulk heat capacity of the hydrogen.

Case 3: Here we consider a less practical case where a cylindrical chunk of unprotected solid hydrogen is floating in-orbit. Such a problem would exist if unprotected solid hydrogen was transferred through the atmosphere from one vehicle to another, or was awaiting rendezvous with a cargo ship. We will assume that no meteorites or atmospheric gases collide with the solid hydrogen, and all sublimed hydrogen is lost forever.

The cylinder of solid hydrogen will be treated as a black body, absorbing the full radiant energy (~ 0.2 W/cm^2) of the sun, earth albedo, planet-shine, etc. The outside surface of the cylinder will quickly come to ~ 5 K and will, therefore, be incapable of appreciable radiation to space (at ~ 4 K). Neglecting the initial 'flashing loss' of ~ 2 percent, we assume that all subsequent sublimation takes place at ~ 5 K. Using the same data as in Case 2, and a thermal heat flux of 0.2 W/cm^2, we calculate a storage duration of 1.082 days. This brief storage interval results because the net heat flux is 2000 times that of Case 2, i.e., $[(0.2)/(10^{-4})]1.082 = 2164$ days as in Case 2.

This short storage interval implies that the mass efflux of hydrogen, away from the cylindrical solid, is sufficiently high to elevate the pressure at the solid-vapor interface. Any increase in pressure, at the subliming interface, is accompanied by an increased temperature in the solid and a modest increase in the heat of vaporization; however, the storage duration would be extended by not more than 25 percent. As vaporization proceeds, the volume/area ratio of the solid cylinder is rapidly reduced -- this effect is far more influential than the modest increase in heat of vaporization (sublimation) and results in much shorter storage times. The reduction in volume/area ratio should more than compensate for any increase in heat of vaporization; therefore, the estimated storage duration for a cylinder of solid hydrogen, 7 m in diameter by 28 m long, is approximately one day.

2.2 Interplanetary space storage

This section can be treated rather lightly because all of the groundwork has been completed. Case 1, for example, transplanted into interplanetary space will be an identical problem, except that the net heat flux will be lower; consequently, the storage times will be longer. The exact storage duration will vary with the position of the storage tank in space, and the incident radiant energy. While the solar radiation is inversely proportional to the square of the distance from the sun, the storage tank may also be exposed to appreciable planet-shine. Thus, in general, the storage duration in space will exceed that computed for Case 1 in earth orbit.

For Case 2, in-space, the net heat flux will be different and the environmental pressure will be lower. Interplanetary space pressure is normally taken as 10^{-12} to 10^{-14} torr in the solar system, and intergalactic space pressure is estimated at 10^{-15} to 10^{-16} torr.

From table 2 we see that 10^{-12} to 10^{-14} torr will produce a temperature of ~ 3 K in the solid hydrogen. We have already considered Case 2 where the solid hydrogen temperature is 5 K. The heat of sublimation is decreased slightly between 5 K and 3 K, producing lower storage times; however, the decrease in radiant heat flux should more than compensate for this effect. Then, for Case 2 we would expect storage durability, in-space, to exceed that of Case 2 in earth orbit.

For Case 3, in-space, we will again attain an equilibrium solid hydrogen temperature of ~ 3 K. The storage duration will be 1/2000 of Case 2 (in-space), and would be expected to exceed that of Case 3 in earth orbit.

For Case 2, in-space, the flashing loss is slightly higher than in a 100 nautical mile earth orbit. From table 2 the flashing loss between 13 K and 3 K is (8.4/409)100 = 2.05 percent.

3. SUMMARY

The significant advantages of subcooled liquid, slush, and solid hydrogen, as space storable propellants, are made evident. Maximum storage duration of hydrogen propellant is obtained by using solid hydrogen and the maximum allowable tank vent pressure. Maximum 'no-loss' storage duration is also obtained by using solid hydrogen. A comparison of storage durability of subcooled liquid, slush, and solid hydrogen is given in table 1.

The bulk density and heat capacity of solid hydrogen are not significantly increased by reducing the temperature of the solid below 13 K. Conversely, the heat of sublimation of solid hydrogen is markedly decreased at temperatures below 13 K. Thus, the storage durability of solid hydrogen is decreased when it is stored at space environment pressures. An uninsulated cylinder of solid hydrogen, 7 m in diameter

by 28 m long, would vaporize in approximately one day in an earth orbit of 185 km. Thus, it is apparent that the use of solid hydrogen will require that the propellant be frozen in-place in well-insulated modular storage units.

4. REFERENCES

1. Ehricke, K. A., A systems analysis of fast manned flights to Venus and Mars, Part II: Storage of liquid and solid hydrogen on nuclear-powered interplanetary vehicles, Journ. of Engr. for Industry, 83, No. 1, 13-28 (Feb. 1961).

2. Vaniman, J. L., Worlund, A. L., and Winstead, T. W., Slush and subcooled propellants for lunar and interplanetary missions, in Adv. in Cryo. Engr. 14, Ed. K. D. Timmerhaus, pp. 20-29 (Plenum Press Inc., New York, N.Y., 1969).

3. Sindt, C. F., A summary of the characterization study of slush hydrogen, Cryogenics, 10, No. 5, 372-379 (Oct. 1970).

4. Staylor, W. F., Frozen propellant - a booster concept? Astron. and Aero., 9, No. 9, 56-59 (Sept. 1971).

5. U.S. STANDARD ATMOSPHERE, 1962, available from superintendent of documents, U.S. Gov. Print. Office, Wash. 25, D.C.

6. Esel'son, B. N., Blagoi, Yu.P., Grigor'ev, V. N., Manzhelii, V. G., Midhailenko, S. A., and Neklyudov, N. P., Properties of liquid and solid hydrogen (translated from Russian, 1971), available from U.S. Dept. of Commerce, National Tech. Inform. Service, Springfield, Va., 22151.

7. Mullins, J. C., Zeigler, W. T., and Kirk, B. S., The thermodynamic properties of parahydrogen from 1° to 22°K, Tech. Report No. 1, Engr. Exper. Station, Georgia Inst. of Tech., Atlanta, Ga., (Nov. 1961).

NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National
Bureau of Standards research and development in physics, mathematics, chemistry, and engineering. Comprehensive scientific papers give complete details of the work, including laboratory data, experimental procedures, and theoretical and mathematical analyses. Illustrated with photographs, drawings, and charts.

Published in three sections, available separately:

● Physics and Chemistry

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, $9.50; foreign, $11.75*.

● Mathematical Sciences

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, $5.00; foreign, $6.25*.

● Engineering and Instrumentation

Reporting results of interest chiefly to the engineer and the applied scientist. This section includes many of the new developments in instrumentation resulting from the Bureau's work in physical measurement, data processing, and development of test methods. It will also cover some of the work in acoustics, applied mechanics, building research, and cryogenic engineering. Issued quarterly. Annual subscription: Domestic, $5.00; foreign, $6.25*.

TECHNICAL NEWS BULLETIN

The best single source of information concerning the Bureau's research, developmental, cooperative and publication activities, this monthly publication is designed for the industry-oriented individual whose daily work involves intimate contact with science and technology—*for engineers, chemists, physicists, research managers, product-development managers, and company executives.* Annual subscription: Domestic, $3.00; foreign, $4.00*.

* Difference in price is due to extra cost of foreign mailing.

NONPERIODICALS

Applied Mathematics Series. Mathematical tables, manuals, and studies.

Building Science Series. Research results, test methods, and performance criteria of building materials, components, systems, and structures.

Handbooks. Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications. Proceedings of NBS conferences, bibliographies, annual reports, wall charts, pamphlets, etc.

Monographs. Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

National Standard Reference Data Series. NSRDS provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated.

Product Standards. Provide requirements for sizes, types, quality and methods for testing various industrial products. These standards are developed cooperatively with interested Government and industry groups and provide the basis for common understanding of product characteristics for both buyers and sellers. Their use is voluntary.

Technical Notes. This series consists of communications and reports (covering both other agency and NBS-sponsored work) of limited or transitory interest.

Federal Information Processing Standards Publications. This series is the official publication within the Federal Government for information on standards adopted and promulgated under the Public Law 89-306, and Bureau of the Budget Circular A-86 entitled, Standardization of Data Elements and Codes in Data Systems.

Consumer Information Series. Practical information, based on NBS research and experience, covering areas of interest to the consumer. Easily understandable language and illustrations provide useful background knowledge for shopping in today's technological marketplace.

NBS Special Publication 305, Supplement 1, Publications of the NBS, 1968-1969. When ordering, include Catalog No. C13.10:305. Price $4.50; foreign, $5.75.

Order NBS publications from:
Superintendent of Documents
Government Printing Office
Washington, D.C. 20402